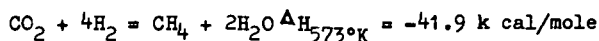
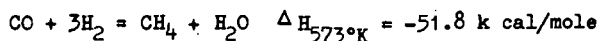


George W Bridger and Colin Woodward

Research Department, Imperial Chemical Industries Limited, Agricultural Division,  
P O Box 6, Billingham, Teesside, TS23 1LE, England

### Introduction

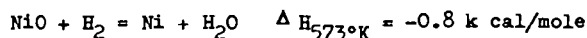
Methanation is the final stage in the purification of synthesis gas in which small concentrations of CO and CO<sub>2</sub> (0.1 - 0.5%) are removed catalytically by reaction with hydrogen:-



The methanation process commonly operates at pressure up to 30 atm and, with the nickel catalyst which is almost universally used for the process, the inlet temperature is about 300°C (570°F). Almost complete conversion of the oxides of carbon occurs giving a product synthesis gas containing less than 5 ppm CO + CO<sub>2</sub>. The temperature rise for the exothermic methanation reactions is typically 35°C (60°F).

### Catalyst Formulation

The catalysts used in the process are essentially nickel metal dispersed on a support material consisting of various oxide mixtures such as alumina, silica, lime, magnesia and compounds such as calcium aluminate cements. When the catalyst is made the nickel is present as nickel oxide which is reduced in the plant converter with hydrogen, usually the 3:1 H<sub>2</sub>:N<sub>2</sub> synthesis gas:-



The heat of reaction is negligible and there is no significant change in temperature in the catalyst bed during reduction. Design limitations in most modern plants require that the catalyst should preferably be reduced at its normal operating temperature, around 300°C (570°F). Once some metallic nickel has been formed, however, methanation begins with the corresponding temperature rise which accelerates reduction of the catalyst further down the reactor. Clearly, the reduction process will continue after the reactor is on-line so that it is common for the activity of the catalyst to continue to increase for some time until an equilibrium state, corresponding to a particular degree of reduction of the nickel, is reached. If engineering considerations permit, the reduction process can be accelerated without detrimental effect upon the catalyst by increasing the temperature to ~660°F.

A good methanation catalyst is one which is physically strong, reducible at 300°C (570°F) and has a high activity. In order to provide a long life, it must retain these properties in use. Commonly lives of 3-5 years are obtained from charges of ICI catalyst 11-3, depending on the temperature of operation and the presence of poisons in the synthesis gas, factors which are discussed later relative to catalyst life. These properties can be obtained by careful attention to the formulation and manufacture of the catalyst.

Methanation activity is related to the surface area of the nickel metal obtained when the catalyst is reduced. The highest surface area of metal and the highest activity are obtained when the nickel is produced as very small crystallites, usually below 100 Å in diameter. One of the functions of the other oxides in the catalyst is to support this fine dispersion of nickel crystallites so that they are available for reaction. The oxides mixed with nickel also retard growth or

sintering of the metal to form large crystallites with a lower surface area and lower activity. The nickel can be dispersed among the other oxides in various ways producing different degrees of mixing e g by impregnation of a preformed oxide support with a soluble nickel compound, or by coprecipitating a nickel compound together with the other materials such as aluminium or magnesium as hydroxides or carbonates. These materials are worked up by drying, decomposing etc and pelleting or extruding precipitated materials, to produce the final catalyst.

Intimate mixing of the components can lead to the formation of compounds or of solid solutions of the components which are difficult to reduce at 300°F but which, when reduced, contain well dispersed and well stabilised nickel. Methanation catalysts in practice therefore are compromises which achieve an optimum reducibility with activity and stability.

An example of compound formation is provided by alumina which, with nickel oxide, readily forms spinel compounds of the type  $\text{NiO} \cdot \text{Al}_2\text{O}_3$ . A temperature around 1000°C (1800°F) is necessary for combination when NiO is mixed with  $\alpha$ - $\text{Al}_2\text{O}_3$  but with finely divided NiO and  $\gamma$ - $\text{Al}_2\text{O}_3$  temperatures around 500°C (930°F) are sufficient. When the oxides are coprecipitated "spinel precursors" can be detected in the dried precipitate and such catalysts have to be reduced at temperatures as high as 500°C (930°F). They are, therefore, unsuitable for use in conventional ammonia synthesis methanation units.

Magnesia forms solid solutions with NiO. Both MgO and NiO have face-centred cubic lattices with NaCl - type structures. The similarity between the ionic radii of the metals ( $\text{Ni}^{2+} = 0.69\text{\AA}$ ,  $\text{Mg}^{2+} = 0.65\text{\AA}$ ) allows interchangeability in a crystal lattice and thus the formation of solid solutions of any proportions of the two oxides is possible. Such solid solutions are more difficult to reduce than separate NiO. Thus Takemura et al (Ref 1) showed that NiO reduced completely in the range 230° - 400°C (440° - 750°F) while a 10% NiO - 90% MgO solid solution reduced in two stages, one in the range 230° - 400°C and the other in the range 500° - 600°C (930° - 1100°F). For ease and completeness of reduction in a methanation catalyst, therefore, excessive solid solution formation should be avoided. As indicated above however solid solution formation is beneficial in retarding crystal growth of NiO during manufacture and of reduced Ni during operation. During manufacture a precipitated nickel compound such as the carbonate has to be converted into nickel oxide and, in order to obtain small NiO crystallites, it is desirable that the calcination temperature should be the minimum compatible with efficient conversion of  $\text{NiCO}_3$  to NiO. Differential thermal analysis (Figure 1) shows that this endothermic process occurs in two main stages with maxima around 150°C (300°F) and 340°C (640°F) and that the presence of a proportion of magnesia in a solid solution raises the required temperature by only about 15°C (25°F).

This presence of MgO, however, does retard the growth of NiO during calcination as shown in figures 2, 3 and 4. Figure 2 shows, for example, that calcination at 500°C (920°F) for 4 hours results in an increase in NiO crystallite size to 300 - 400 Å whereas, after the same treatment, the crystallite size of an NiO-MgO solid solution (60 - 40 w/w) would be only about 80 Å. Figures 3 and 4 show the effect of duration of calcination on crystal growth at different temperatures. Crystallite size is proportional to  $T^{0.25}$  for NiO alone, and proportional to  $T^{0.12}$  for NiO-MgO and for MgO alone.

Figure 5 shows the effect of calcination temperature on the subsequent activity of the catalyst after reduction at 300°C (570°F). These activity measurements are made in laboratory tubular reactors operating at 1 atmosphere pressure, inlet gas composition CO 0.40%,  $\text{N}_2$  25%,  $\text{H}_2$  74.6% and inlet temperature 300°C. Conversion of CO is measured and the catalyst activity expressed as the activity coefficient, k, in the first order equation :

$$\text{rate} = k p_{\text{CO}} P^{0.3} \left(1 - \frac{K}{K_p}\right) e^{-\frac{e}{RT}}$$

The reducibility of the catalyst is demonstrated in Figure 6 which shows the activity of catalysts, measured as described above, after reduction to constant activity at temperatures in the range 280° - 350°C (530° - 660°F). It will be seen that catalyst 11-3 compares favourably with other catalysts which contain larger amounts of alumina and consequently are more difficult to reduce at acceptable temperatures.

In summary, therefore, we have found it beneficial to include a small amount of MgO (2 - 3%) in ICI methanation catalyst 11-3. This provides the ideal compromise between ease of reducibility and sintering resistance. By this means, a catalyst is produced which is readily reduced at 300°C - 350°C (570° - 660°F) but with which loss of activity caused by sintering is not a problem during several years' normal operation at temperatures up to 350°C (660°F). This good performance has been confirmed by experience in many plants including ICI's three 1000 ton/day ammonia plants at Billingham, England.

#### Poisons

With a well constituted catalyst of this type, at normal operating temperatures sintering is not an important cause of loss of activity even if the catalyst is occasionally overheated. The principal cause is poisoning. Sulphur compounds are virulent poisons for nickel catalysts but in the synthesis gas purification stream the methanation catalyst is protected by the LT shift catalyst in the preceding stage which is an efficient sulphur-guard. Therefore in normal operation the methanation catalyst is unlikely to be exposed to sulphur. The exception to this would be if the LT shift converter were partially by-passed in which instance sulphur could reach the methanation catalyst. Serious deactivation of the catalyst can occur; for example one containing about 30% NiO (before reduction) shows significant loss of activity when the sulphur content exceeds ~0.1%.

The poisons most likely to be encountered on an ammonia plant are those originating in the CO<sub>2</sub>-removal system which precedes the methanator. Carry-over of a small amount of liquid into the methanator, which is almost inevitable, is not normally serious. Plant malfunction, however, can sometimes result in large quantities of CO<sub>2</sub>-removal liquor being pumped over the catalyst and this can be very deleterious. Table 1 shows the effect of common CO<sub>2</sub> - removal liquors on methanation catalyst activity.

Table 1                      Poisoning effects of CO<sub>2</sub> removal systems

Process	Chemicals	Effect
Benfield process	Aqueous potassium carbonate	Blocking of pores of methanation catalyst by evaporation of potassium carbonate solution
Vetrocoke process	Aqueous potassium carbonate-arsenious oxide	As Benfield. Also As <sub>2</sub> O <sub>3</sub> is poison - about one-half of activity is lost when As = 0.5%
Benfield DEA	Aqueous potassium carbonate plus 3 per cent diethanolamine	As Benfield. DEA is harmless
Sulphinol	Sulpholane, water, di-iso-propanolamine	Sulpholane will decompose and give sulphur poisoning
MEA, DEA	Mono- or diethanolamine in aqueous solution	No poisoning effect
Cold Rectisol	Methanol	No poisoning effect

## Prediction of Catalyst Life

In the operation of a methanator, it is important to be able to estimate the remaining future useful life of a catalyst charge at any moment. The question to be answered is "should this catalyst charge be changed during the shut-down planned for x weeks time or is it good enough to last until the next shut-down planned for a year hence?". Strictly, therefore, the requirement is for a Yes/No answer rather than a precise prediction, the assumption being that changing a catalyst alone will never be the reason for a shutdown. This is reasonable because, if the cost of plant down-time is compared with the cost of a catalyst charge, it is clearly economic to change catalyst rather than to run the risk of a catalyst failure causing an additional shut-down.

Methanation converters on most ammonia plants are over-designed, both for safety reasons and as a result of increases in catalyst activity since plants were built. Consequently at the beginning of the catalyst's life most of the methanation is virtually completed in the first 25% of the bed and monitoring exit gas composition gives no information about die-off of the catalyst. Catalyst deactivation occurs normally by a poisoning mechanism and, as poisoning continues, the volume of active catalyst remaining will eventually be insufficient to meet the required duty. Although the thermodynamic exit levels of CO and CO<sub>2</sub> are about 10<sup>-4</sup> ppm, in practice these are not attained because of kinetic and other limitations and the actual exit concentrations, during normal operation, are of the order of 1-2 ppm.

A technique has been devised for calculating when exit carbon oxides will exceed any given design level and hence predicting the future useful life of the catalyst charge. The method is based upon accurate measurement of the temperature profile in the bed using a moveable thermocouple or a series of fixed thermocouples. A point on the profile is selected at which conversion is nearly complete. This point can, for example, be taken as the point at which 5°F temperature rise remains; the total temperature rise across a methanator is typically 60°F. The 5°F point provides a good compromise between selecting a point near the top of the temperature rise, so that pressures and temperatures can be regarded as nearly constant for the remainder of the bed, and minimising inaccuracies in temperature measurements. Obviously, if the method is valid, any selected point will give the same result. The method also assumes that CO methanates before CO<sub>2</sub>, which is commonly accepted (Ref 2), so that over the last part of the catalyst bed, only the completeness of CO<sub>2</sub> methanation need be considered.

The temperature profile obtained by means of a moveable thermocouple is of the form shown in Figure 7. For highest accuracy, the maximum possible number of readings should be made in the region of the 5°F point. Interpretation of this profile to obtain a catalyst life prediction is made graphically and the mathematical derivation of the technique appears in the Appendix. The method assumes first order reaction kinetics with respect to CO<sub>2</sub> (Ref 2). If the gradient of the temperature profile at the 5°F point is drawn, i.e. the tangent to the curve at this point, this is a measure of the rate of reaction at this point in the bed. If catalyst activity is assumed to be constant in the remainder of the bed, this can be used to estimate the further depth of bed required for reaction to reach any selected carbon oxides level. Design limits may be imposed by the requirement to have total CO + CO<sub>2</sub> low enough to avoid poisoning ammonia synthesis catalyst (e.g. CO + CO<sub>2</sub> < 10 ppm).<sup>2</sup> More commonly, however, the main objective is to minimise ammonium carbamate, NH<sub>4</sub>COONH<sub>2</sub>, in the synthesis gas loop for which a limit of CO<sub>2</sub> < 2 ppm appears desirable.

The last 5°F rise of temperature at the end of the bed corresponds to methanation of about 465 ppm CO<sub>2</sub>; typically methanation of 1% CO<sub>2</sub> produces a temperature rise of 108°F; 1% CO produces 133°F. It can be shown (see Appendix) that an exit level of 2 ppm CO<sub>2</sub> corresponds to the point at which the tangent intersects a horizontal line drawn 28°F above the 5°F point. The graphical constructions are therefore as shown in Figure 8. This permits identification of the present position of the "effective end of the bed" and hence of the amount of reserve

catalyst remaining. In our experience, the "effective end of the bed" is usually located by this method as 1-1.5 ft below the point at which, within measurement accuracy, maximum temperature is attained. This figure obviously depends upon the shape of the profile, i.e. on the activity of the catalyst, and should be regarded as not more than an indication. It is then necessary to study the previous history of the charge in order to estimate the rate of profile movement and likely future useful life of the charge.

The main disadvantage of this technique is that it relies upon very accurate temperature measurement, particularly near the top of the temperature profile so that the position of the 5°F point can be established and the tangent accurately constructed. Also, the end of the bed is predicted from only kinetic considerations when, in fact, other factors may be more important. In practice, however, although this introduces some scatter into successive measurements - as does variation in duty required of the methanator - the technique has proved very satisfactory. Typical findings are represented in Figure 9 where, if the present rate of catalyst die-off continues, the end of useful catalyst life is reached when the current end of the bed reaches the actual end of the bed, in this instance after about 6 years on line.

### Conclusion

In summary, therefore, we can say that methanation catalysts for these applications are very satisfactory in terms of activity, strength and stability. In the absence of detrimental mal-operations, one can expect favourable operating experience and we have demonstrated a simple and convenient method by which the future useful life of a catalyst on-line can be estimated.

### Acknowledgements

We are pleased to acknowledge our indebtedness to colleagues Dr P J Baldock and Mr A Parker for the X-ray crystallographic studies, to Dr P Snowden who devised the life prediction technique and to Imperial Chemical Industries Ltd. for permission to publish this paper.

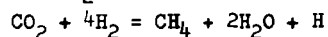
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- 1 Y Takemura, Y Morita and K Yamamoto, Bull. Jap. Petrol. Inst., **9**, 13, (1967)
- 2 T Van Herwijnen, H Van Doesburg and W A De Jong, J Catal., **28**, 391, (1973)

### Appendix

#### Derivation of Graphical Method

The CO<sub>2</sub> methanation reaction is:-



where H = heat of reaction

The rate of conversion of CO<sub>2</sub> in a short section of the catalyst bed of length dl can be calculated from the first order rate equation:-

$$dX = k_o p P^a \left[ 1 - f\left(\frac{K}{K_p}\right) \right] e^{-\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right)} \dots \dots \dots 1)$$

where dX = moles CO<sub>2</sub> converted per second per unit volume of bed

$k_o$  = rate constant at  $T_o$   
 $p$  = partial pressure of  $CO_2$   
 $P$  = total pressure  
 $T$  = temperature of section of bed, °K  
 $a$  = total pressure coefficient  
 $K_p$  = equilibrium constant for the reaction  
 $K = \frac{(p_{CH_4})(p_{H_2O})^2}{p(P_{H_2})^4}$

Since the system is far from equilibrium, (the actual  $CO_2$  concentration even at the exit of the bed is about 2 ppm compared with an equilibrium concentration of  $10^{-4}$  ppm),  $K$  is small compared with  $K_p$  and the term  $\left[1 - f\left(\frac{K}{K_p}\right)\right]$  becomes unity

i.e. the effect of the reverse reaction can be ignored. Equation (1) then becomes:-

$$dX = k_o p P^a e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)} \dots \dots \dots 2)$$

Considering the small section of bed of length  $dl$  and cross-sectional area  $A$ :-  
Heat from reaction =  $dX.HA.dl$  cals/second  
Therefore the temperature rise  $dT$  across the section of bed is given by:-

$$dT = \frac{dX.HA.dl}{GC} \dots \dots \dots 3)$$

where  $G$  = gas flow rate in moles/second

$C$  = specific heat of gas per mole at  $T$  and  $P$

Rearranging (3) and combining with (2):-

$$dX = \frac{C}{H} \frac{G}{A} \frac{dT}{dl} = k_o p P^a e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)}$$

The temperature gradient at a point in the bed where the temperature is  $T$  is therefore:-

$$\frac{dT}{dl} = \frac{HA}{CG} \cdot k_o P^a p e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)}$$

Now for a point A near the top of the profile (see Fig 8) at temperature  $T_1$ , the temperature gradient  $\left(\frac{dT}{dl}\right)_1$  is given by:-

$$\left(\frac{dT}{dl}\right)_1 = \left(\frac{HA}{CG}\right)_1 k_o P_1^a p_1 e^{-\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_o}\right)}$$

Now substituting for  $k_o$  in equation (2),

$$dX = \left(\frac{dT}{dl}\right)_1 \left(\frac{CG}{HA}\right)_1 \frac{P^a p e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)}}{P_1^a p_1 e^{-\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_o}\right)}}$$

Considering only the last section of the bed where little conversion occurs, several simplifications can be made. The total pressure is virtually constant and  $P_1 = P$

$$\text{Hence, } dX = \left(\frac{dT}{dl}\right)_1 \left(\frac{CG}{HA}\right)_1 \frac{P}{P_1} e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)} \dots \dots \dots 4)$$

The temperature change is also small so that the exponential term can be taken as unity. The molar flow,  $G$ , can be assumed to be constant between A and B and the  $\text{CO}_2$  conversion is proportional to the change of  $\text{CO}_2$  partial pressure,  $dp$ . The volume of the section of bed is  $Adl$  so that the rate of  $\text{CO}_2$  conversion,  $dX$ , is therefore:-

$$dX = \frac{G}{Adl} \cdot \frac{dp}{P}$$

Combining this with (4), after simplification:-

$$\frac{dp}{P} = \left(\frac{dT}{dl}\right)_1 \cdot \frac{C}{H} \cdot \frac{P}{P_1} \cdot dl$$

Integrating between A and C, we obtain

$$\ln \frac{P_2}{P_1} = \left(\frac{dT}{dl}\right)_1 \cdot \frac{C}{H} \cdot \frac{P}{P_1} (L_2 - L_1) \dots \dots \dots 5)$$

where  $P_2$  = partial pressure of  $\text{CO}_2$  at bed depth  $L_2$

For a typical methanation system,

$$C = 4 \times 10^{-3} \text{ k cal/mole } ^\circ\text{F}$$

$$H = -41.9 \text{ k cal/mole}$$

$$P = 30 \text{ at}$$

Taking A as the point  $5^\circ\text{F}$  below maximum temperature, at this point, 465 ppm  $\text{CO}_2$  remains to be methanated. Take design exit  $\text{CO}_2$  concentration as 2 ppm. Equation (5) reduces to:-

$$2.303 \log_{10} \left(\frac{2}{465}\right) = -\left(\frac{dT}{dl}\right)_1 \times \frac{4 \times 10^{-3}}{41.9} \times \frac{1}{465 \times 10^{-6}} (L_2 - L_1)$$

$$(L_2 - L_1) = \frac{28.0}{\left(\frac{dT}{dl}\right)_1}$$

$$\text{Since } \left(\frac{dT}{dl}\right)_1 = \frac{T_2 - T_1}{L_2 - L_1}$$

$$T_2 - T_1 = 28.0 ^\circ\text{F}$$

Hence a line drawn  $28^\circ\text{F}$  above the  $5^\circ\text{F}$  point will intersect the tangent to the profile at the  $5^\circ\text{F}$  point at the position corresponding to the present end of the catalyst bed.

FIGURE 1. D.T.A. CURVES OF BASIC CARBONATES

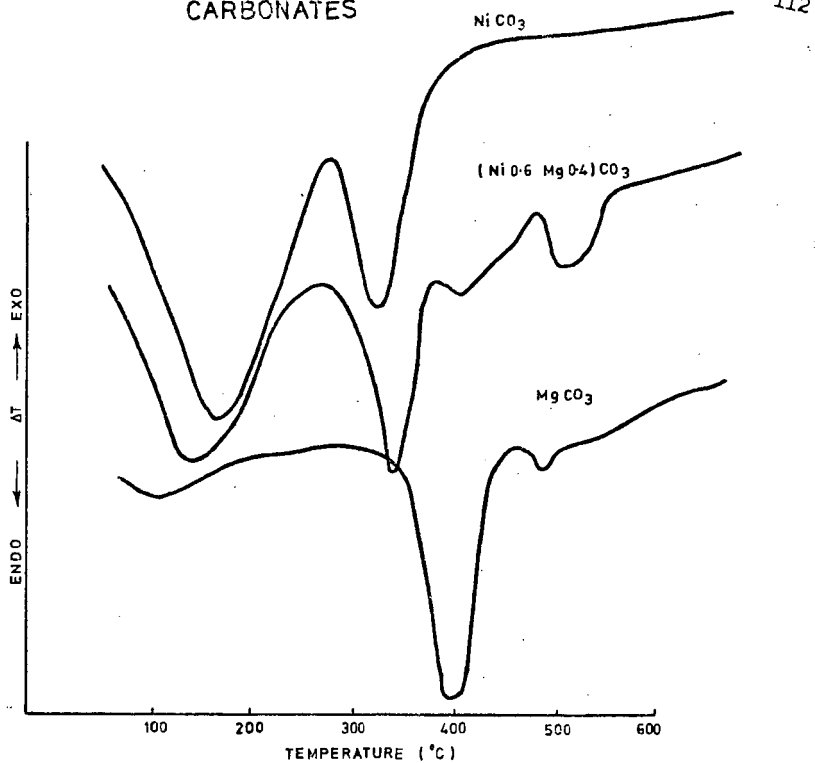


FIGURE 2. VARIATION OF CRYSTALLITE SIZE WITH CALCINATION TEMPERATURE

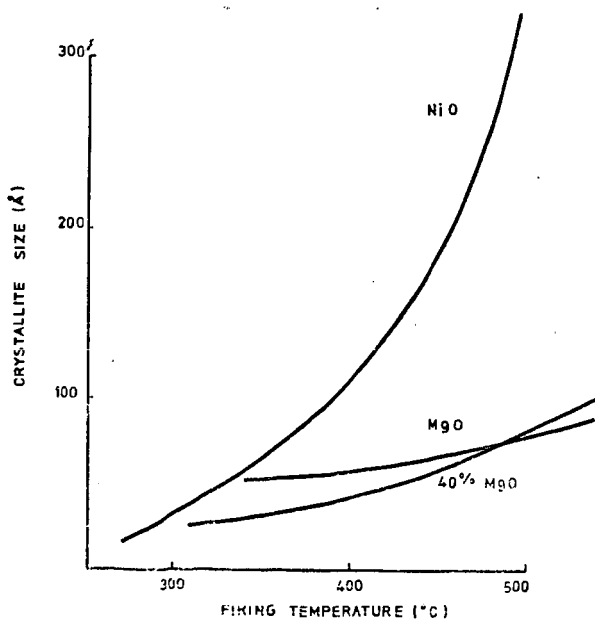




FIGURE 4. VARIATION OF NiO-40% MgO CRYSTALLITE SIZE WITH TIME

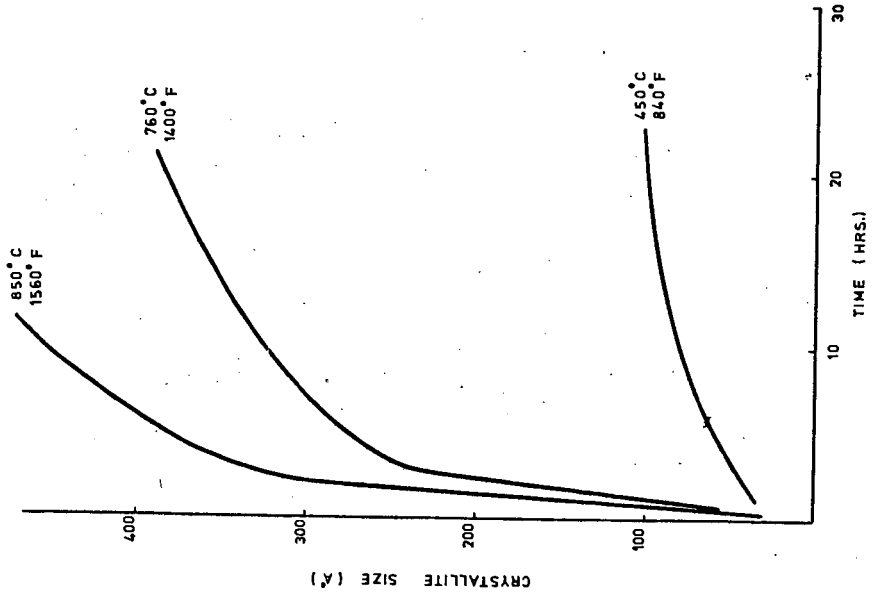


FIGURE 3. VARIATION OF NiO CRYSTALLITE SIZE WITH TIME

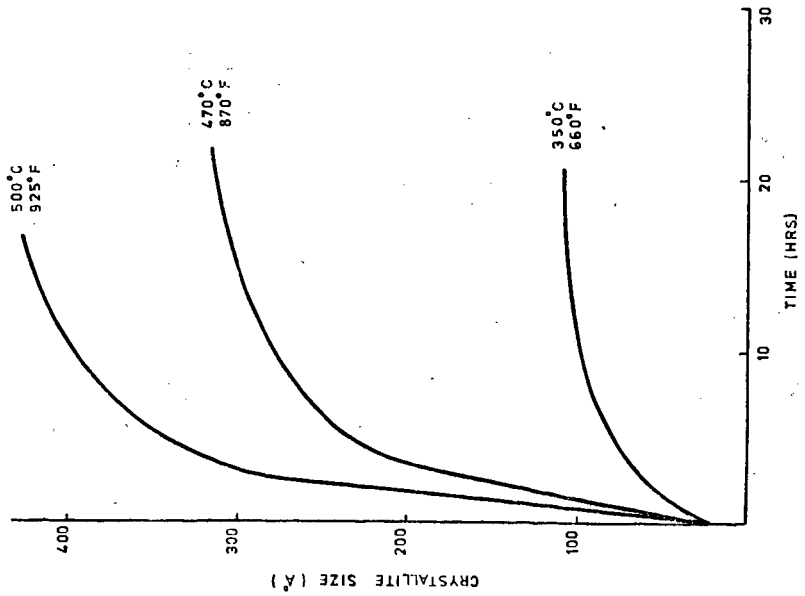


FIGURE 5. ACTIVITY vs CALCINATION TEMPERATURE

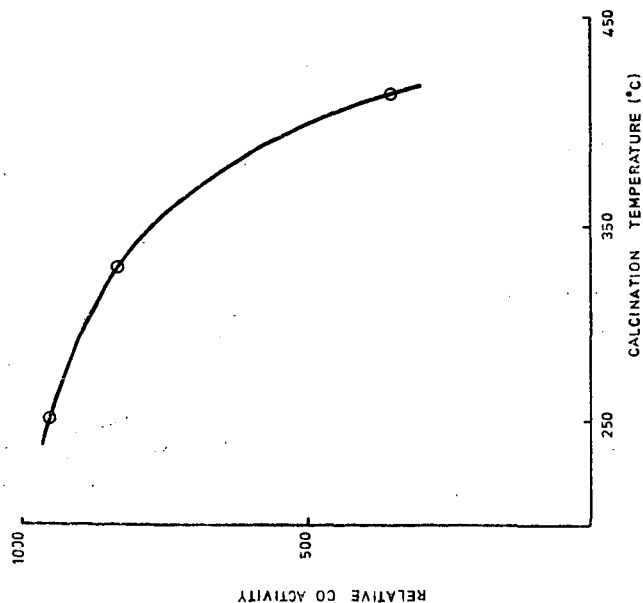


FIGURE 6. ACTIVITY vs REDUCTION TEMPERATURE

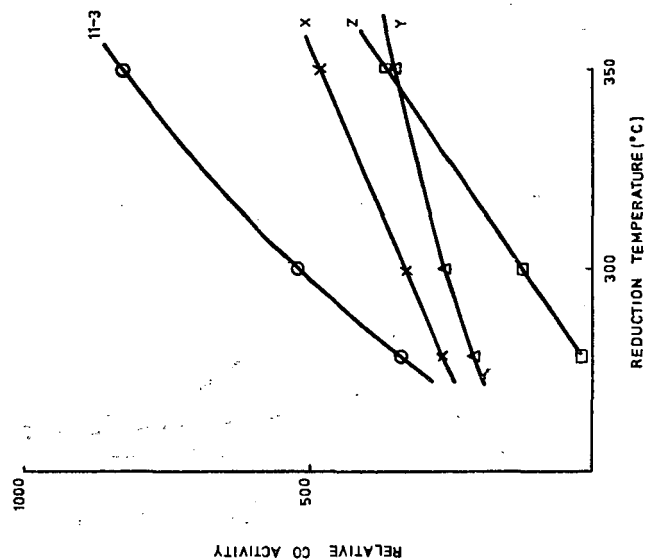


FIGURE 7. TYPICAL METHANATOR TEMPERATURE PROFILE

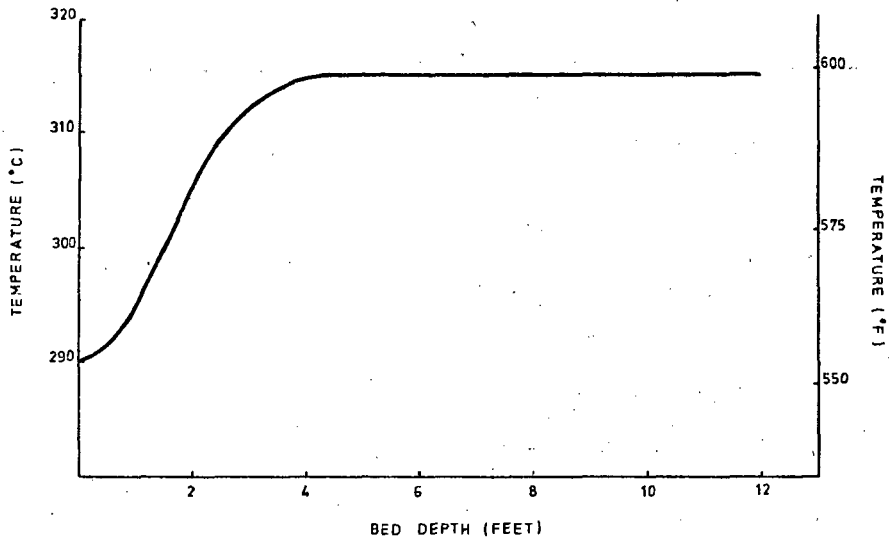


FIGURE 8. LOCATION OF EFFECTIVE END OF BED

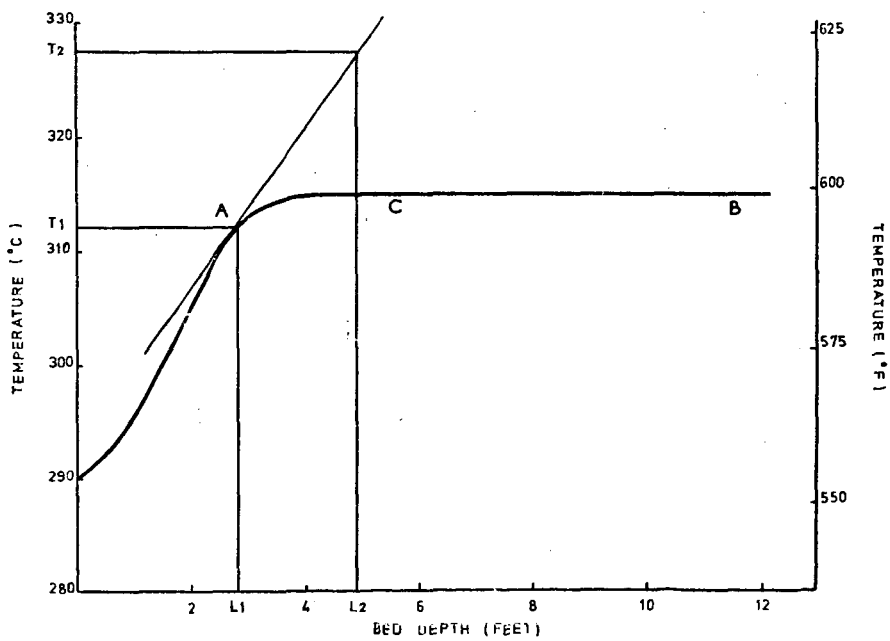


FIGURE 9. FUTURE USEFUL LIFE PREDICTION

